Kinetic studies on visible light-assisted degradation of acid red 88 in presence of metal-ion coupled oxone reagent

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Abstract

Visible light-assisted photo-Fenton-like oxidation of a mono-azo textile dye, acid red 88 (AR88), has been carried out in presence of Cu^{2+} or Fe^{3+} ions as the catalyst and oxone as the oxidant. The optimal concentrations of metal-ion (Cu^{2+} or Fe^{3+}) and oxidant (oxone) for the abatement of the azo dye were determined. Decolorization of AR88 in Cu^{2+}/oxone system was found to follow zero-order kinetics with respect to the dye and first-order kinetics when Fe^{3+}/oxone system was employed. In both the cases, the decolorization of AR88 was found to be accelerated with increasing concentrations of metal-ions in solution. Almost 95% decolorization was attained in 2 h with Cu^{2+} ion and within 14 min with Fe^{3+} at each metal-ion concentration of 0.075 mM. Mineralization studies were also carried out by monitoring the reduction of total organic carbon (TOC) content during the course of the reaction. A suitable mechanism has been proposed to explain the observed kinetics of decolorization of AR88 in both the Fe^{3+}/oxone and Cu^{2+}/oxone systems.

1. Introduction

Degradation of organic pollutants like dyes in industrial wastewater has become increasingly important during the last decade in the field of advanced oxidation processes (AOPs) [1–5]. AOPs are attractive because they holdout the promise of completely mineralizing the target pollutant. AOPs essentially involve the generation of •OH, a powerful and non-selective oxidizing agent that can be produced by different combinations of ozone, hydrogen peroxide, UV radiation and titanium dioxide and also by the combination of hydrogen peroxide with ferrous ion in the Fenton's reagent, for the destruction of hazardous pollutants in air and water. The rate of degradation of the organic pollutants by Fenton reaction increases in the presence of an irradiation source. While direct photolysis of O_3

or H_2O_2 needs photons of shorter wavelengths (<310 nm), TiO_2 photocatalyses the reaction even at 380 nm [6], and photo-Fenton reactions can use photons with wavelength close to 400 nm. The mixtures $Fe^{3+} + H_2O_2$ (known as Fenton-like reagents) have shown photon absorption up to 550 nm [7–9]. Photo-Fenton processes, thus, are a potential cost-effective AOP that can be run under solar irradiation [10–12].

Oxone (HSO_5^-), a mono-SO_3^- substituted hydrogen peroxide (HOOH), is a powerful oxidizing agent [$E° = 1.82$ V vs. standard hydrogen electrode (SHE)], which undergoes radiolytic and photolytic reactions [13,14] but no photochemical decomposition unless it is irradiated in the UV region with the wavelength ≤ 260 nm. However, in the presence of photocatalysts efficient decomposition of oxone has been observed with light of wavelength ≤ 390 nm. Photocatalytic decomposition of oxone in the presence of some semiconductors like WO_3, Bi_2O_3 and Fe_2O_3 [15–17] and transition metal-ions like Mn^{2+} [18], Cu^{2+} [19], Co^{2+} [20–23] and Ru^{3+} [24], has also been reported.

Removal of acid red 88 (AR88) from contaminated water using various methods [25–30] like biological degradation involving *Spingomonas* sp. strain 1CX, adsorption by neutral alumina, photocatalytic oxidation and ozonation were reported.

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So, our intention is to apply oxone as an alternative oxidant for the photo-Fenton oxidation of acid red 88 and achieve higher degradation and mineralization rate. Oxone is a suitable choice owing to its higher oxidation potential than H_2O_2 ($E°_{H_2O_2} = 1.76$ V; $E°_{oxone} = 1.82$ V) and also in the presence of metal-ions, oxone is known to generate radical species such as $SO_4^{•-}$ and $SO_5^{•-}$ in aqueous medium in addition to $^•OH$ through the radical chain reactions leading to the enhanced mineralization of target pollutants.

2. Experimental

2.1. Materials

Acid red 88, the textile dye with the molecular formula $C_{20}H_{13}N_2O_4SNa$, which absorbs in the visible region ($\lambda_{max} = 506$ nm; $\varepsilon_{506} = 1.55 \times 10^4$ M^{-1} cm^{-1}), is used as a substrate. Solutions of Fe^{3+} and Cu^{2+} ions were prepared from analytical grade samples of $Fe(NO_3)_3·9H_2O$ (Merck) and $CuSO_4·5H_2O$ (S.d. fine). Potassium peroxomonosulphate (oxone), a triple salt with the composition $2KHSO_5·KHSO_4·K_2SO_4$ from Janssen Chimica (Belgium) was used as received. Single distilled water from Kilburn Manesty was redistilled over alkaline permanganate and used for all the experiments. When preparing the molar solution of the oxidant, the fact that 1 mol of oxone contains 2 mol of peroxomonosulphate is taken into account as shown by its chemical formula.

2.2. Irradiation procedures

The solar simulated light irradiation was carried out on borosilicate glass reactor vessel (100 ml) with appropriate combination of solutions such as the dye, metal-ion and oxone. Oxone was always added to the solution in the reactor vessel at the end before irradiation and the natural pH of the solution was found to be around 2.8 ± 0.1. Light irradiation was carried out by means of a solar box which consists of three 250 W tungsten–halogen lamps (irradiation intensity: $80,600 \pm 10$ lux, Philips, India) inside a rectangular box fitted with two exhaust fans to considerably reduce the increase of temperature (40 °C) due to irradiation inside the solar box. Since the reported decolorization products of AR88, viz., 4-aminonaphthlene sulfonic acid and *o*-nitroso naphthol [27] do not absorb at 506 nm, the decrease in the concentration of the dye was determined spectrophotometrically using UV–vis spectrophotometer (Shimadzu, model: UV-1601) by following the absorbance of the dye solution at 506 nm. Total organic carbon (TOC) content was measured with Thermo Euroglas, model TOC1200, total organic carbon analyzer (Thermo Electron Corporation) calibrated with standard solutions of potassiumhydrogenphthalate. TOC_0 and TOC_t indicate the TOC obtained at initial and various irradiation times.

3. Results and discussion

Control experiments revealed neither the occurrence of decolorization nor mineralization of AR88 in the presence of Fe^{3+} or Cu^{2+} ions alone either in dark or under light irradiation. These experiments also indicated that there are no appreciable decolorization of AR88 in presence of oxone and the metal-ions in the absence of light. In the presence of oxone alone only ca. 16% and ca. 43% of decolorization were observed after 1 and 3 h of visible light irradiation respectively whereas higher decolorization rates could be achieved in the combinations of metal-ion/oxone as depicted in Fig. 1. The UV–vis spectral changes observed during the degradation of AR88 in the presence of Cu^{2+}/oxone and Fe^{3+}/oxone systems under illumination are depicted in Fig. 2. The absorption peak of the dye diminished and disappeared completely under the visible light irradiation in the presence of metal-ion in conjunction with oxone.

3.1. Fe^{3+}/oxone system

3.1.1. Kinetics

Optimization of the catalyst and the oxidant is necessary to apply any process economically viable. In all the experiments with Fe^{3+}/oxone system, the decolorization is observed to follow a first-order reaction with respect to [AR88] (Eq. (1)):

$$\ln\left(\frac{C_0}{C_t}\right) = k't \qquad (1)$$

where C_t and C_0 refer the concentrations of the dye at time 't' and at initial time and k' is the pseudo-first-order rate constant. A straight line passing through the origin was observed when $\ln(C_0/C_t)$ was plotted against t conforming the assumed first-order kinetics as shown in Figs. 1 and 4. The slope of the plots yielded the pseudo-first-order rate constants (k'), which were used in the optimization of concentrations of Fe^{3+} ion and oxone for the decolorization of AR88.
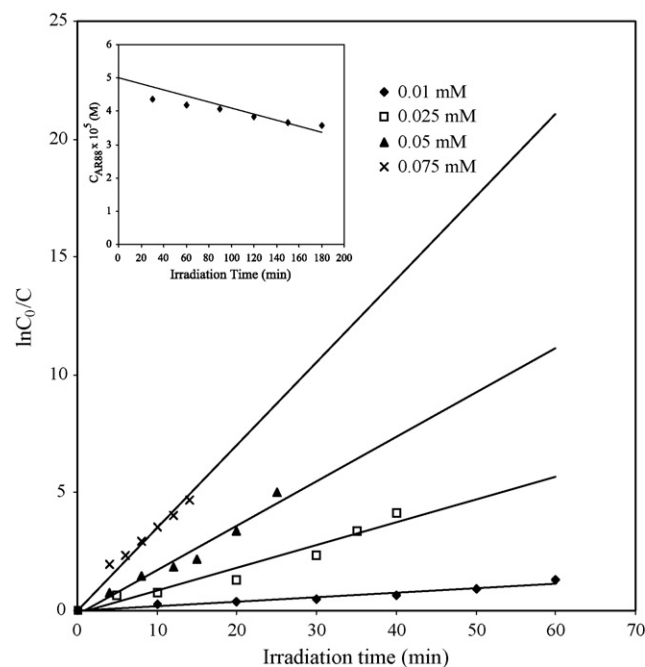

Fig. 1. Decolorization of acid red 88 solutions at different Fe^{3+}-ion concentrations: $C_{AR88} = 0.05$ mM; $C_{oxone} = 5$ mM. Inset shows the degradation rate ($k'_0 = 1.97 \times 10^{-9}$ M s^{-1}) in the absence of Fe^{3+} ion.
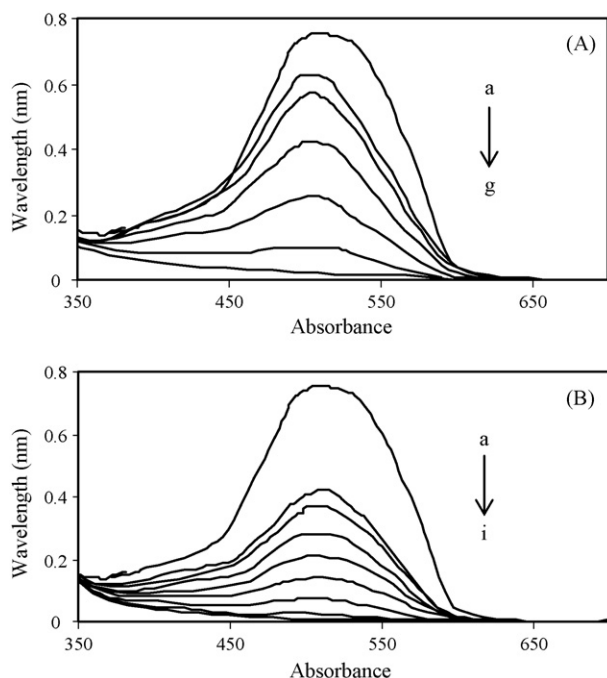
Fig. 2. UV–vis spectral changes observed during the photo-Fenton degradation of acid red 88. (A) $C_{AR88} = 0.05$ mM; $C_{Cu^{2+}} = 0.025$ mM; $C_{oxone} = 5$ mM: (a) 0 min; (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min; (f) 150 min; (g) 180 min. (B) $C_{AR88} = 0.05$ mM; $C_{Fe^{3+}} = 0.025$ mM; $C_{oxone} = 5$ mM: (a) 0 min; (b) 5 min; (c) 10 min; (d) 15 min; (e) 20 min; (f) 25 min; (g) 30 min; (h) 35 min; (i) 40 min.

3.1.2. Effect of Fe^{3+}

In order to elucidate the effect of Fe^{3+} concentration on the decolorization of the dye, a series of experiments were carried out by varying the concentration of Fe^{3+} ion from 0.01 to
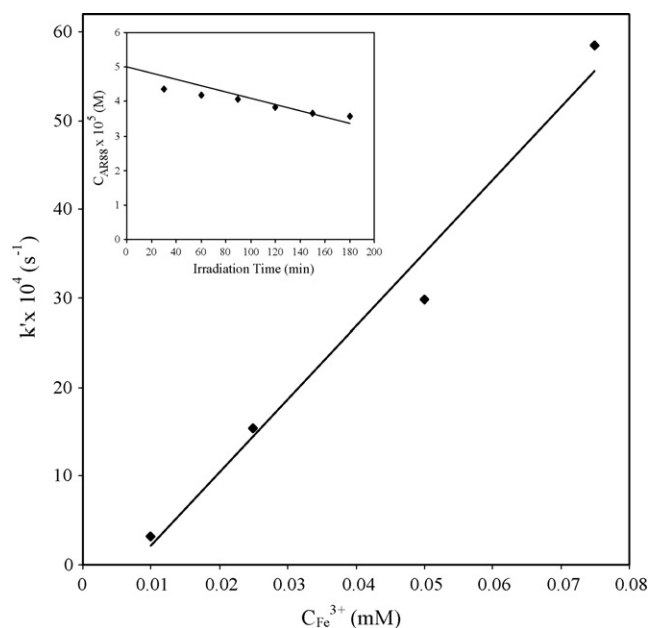

Fig. 3. Plot of pseudo-first-order rate constant as a function of Fe^{3+}-ion concentration for the decolorization of acid red 88 solutions with 5 mM oxone. See inset of Fig. 1 for the degradation rate ($k'_0 = 1.97 \times 10^{-9}$ M s^{-1}) in the absence Fe^{3+} ion.
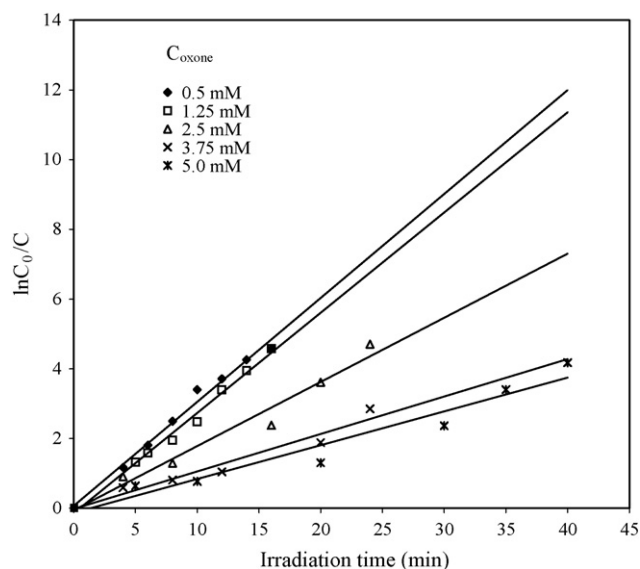

Fig. 4. Decolorization of acid red 88 solutions at different oxone concentrations: $C_{AR88} = 0.05$ mM; $C_{Fe^{3+}} = 0.025$ mM.

0.075 mM while keeping the other experimental parameters constant, viz., $C_{AR88} = 0.05$ mM; $C_{oxone} = 5$ mM. It can be observed that the addition of higher amounts of Fe^{3+} ion considerably decreases the irradiation time required for maximum decolorization. For example, almost 95% decolorization was attained in cal. 14 min at 0.075 mM Fe^{3+}-ion concentration. Fig. 3 shows the variation of pseudo-first-order rate constant (k') as a function of Fe^{3+}-ion concentration. It can be noted that the efficiency of the decolorization increases with increasing concentration of Fe^{3+} ion, which may be attributed to the increased generation of $^{\bullet}OH$ [31–34] by the photolysis of $Fe(OH)^{2+}$ as shown in Eq. (2):

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (2)$$

3.1.3. Variation of oxone concentration

One of the significant experimental parameters to be obtained in the photo-Fenton oxidation process is the optimum concentration of oxidant (oxone) for the maximum decolorization efficiency. In order to understand the effect of oxone concentration on the photocatalyzed degradation of AR88, the concentration of oxone was varied from 0.5 to 5 mM maintaining constant concentrations of dye (0.05 mM) and Fe^{3+} ion (0.025 mM). It was found that there exists a strong oxidant dependence factor for the photodegradation of AR88 using Fe^{3+}/oxone reagent. Also, it can be understood from the plot of k' vs. C_{oxone} (Fig. 5) that the rate constant initially increases with increasing concentration of oxone and then decreases with increase in the C_{oxone}. That is, greater decolorization efficiency was attained when the minimum C_{oxone} was used in our experiment, viz., 0.5 mM. The oxidation rate was negatively affected when the concentration of oxone was further increased which may be due to the scavenging of sulphate and hydroxyl radicals
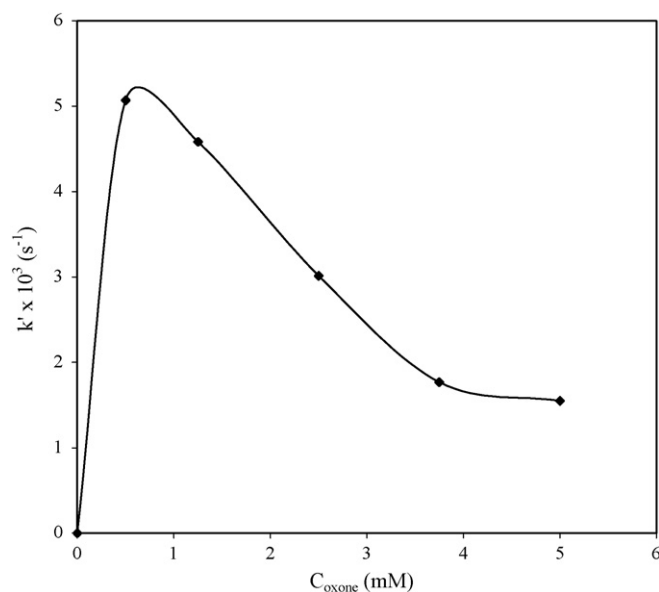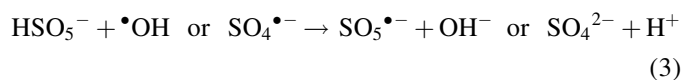
Fig. 5. Plot of pseudo-first-order rate constant as a function of oxone concentration for the decolorization of acid red 88 (0.05 mM) in presence of Fe^{3+} ion (0.025 mM).

Fig. 6. Decolorization of acid red 88 solutions at different Cu^{2+}-ion concentrations: $C_{AR88} = 0.05$ mM; $C_{oxone} = 5$ mM.

by HSO_5^- and the formation of less reactive $SO_5^{\bullet-}$ [8,35] based on Eq. (3):

$$HSO_5^- + {}^\bullet OH \text{ or } SO_4^{\bullet-} \rightarrow SO_5^{\bullet-} + OH^- \text{ or } SO_4^{2-} + H^+$$

(3)

3.2. Cu^{2+}/oxone system

3.2.1. Kinetics

Decolorization of AR88 in Cu^{2+}/oxone system occurred through a zero-order kinetics with respect to the dye (Eq. (4)):

$$C_t = -k_0' t + C_0$$

(4)

where C_0 and C_t denote the concentration of the dye at time $t = 0$ and at various irradiation times and k_0' is the pseudo-zero-order rate constant. The plot of C_t vs. t (Figs. 6 and 8) gave a straight line with negative slope conforming to zero-order kinetics and the slope of the line corresponds to the pseudo-zero-order rate constant. The effect of the concentrations of Cu^{2+} ion and oxone on the photo-Fenton-like degradation of AR88 was determined from the values of pseudo-zero-order rate constant, k_0', at different concentrations of Cu^{2+} ion and oxone.

3.2.2. Variation of Cu^{2+}-ion concentration

The effect of Cu^{2+}-ion concentration on the decolorization of the dye was obtained by varying $C_{Cu^{2+}}$ (0.01–0.075 mM) while keeping the other parameters ($C_{AR88} = 0.05$ mM; $C_{oxone} = 5$ mM) constant. Fig. 7 shows the plot of pseudo-zero-order rate constant (k_0') as a function of Cu^{2+}-ion concentration. It can be observed that the rate of the decolorization does not increase proportionately with increase

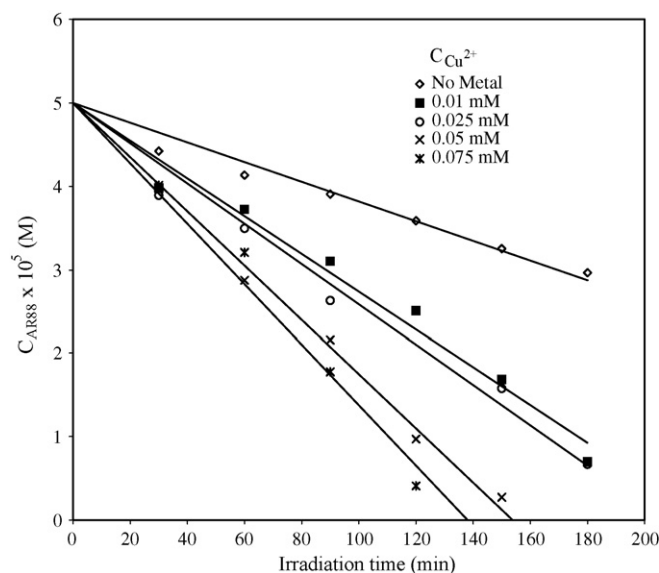in the concentration of Cu^{2+} ion contrary to the observation made in the case of Fe^{3+} ion. However, a definite catalytic effect due to the presence of Cu^{2+} ion was shown by an almost twofold increase in the degradation rate even at $C_{Cu^{2+}}$ of 0.01 mM in comparison to that in the absence of Cu^{2+} ion. Moreover, the addition of higher $C_{Cu^{2+}}$ greatly reduces the irradiation time required for the complete decolorization. For example, about 84% decolorization was obtained in 3 h of visible light irradiation with 0.01 mM Cu^{2+} ion whereas about 95%
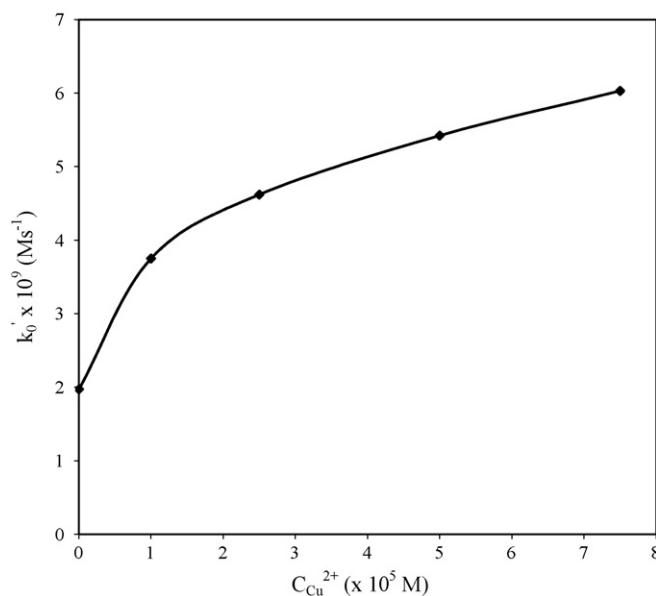

Fig. 7. Plot of pseudo-zero-order rate constant as a function of Cu^{2+}-ion concentration for the decolorization of acid red 88 (0.05 mM) at 5 mM oxone. See inset of Fig. 1 for the degradation rate ($k_0' = 1.97 \times 10^{-9}$ M s^{-1}) in the absence Cu^{2+} ion.

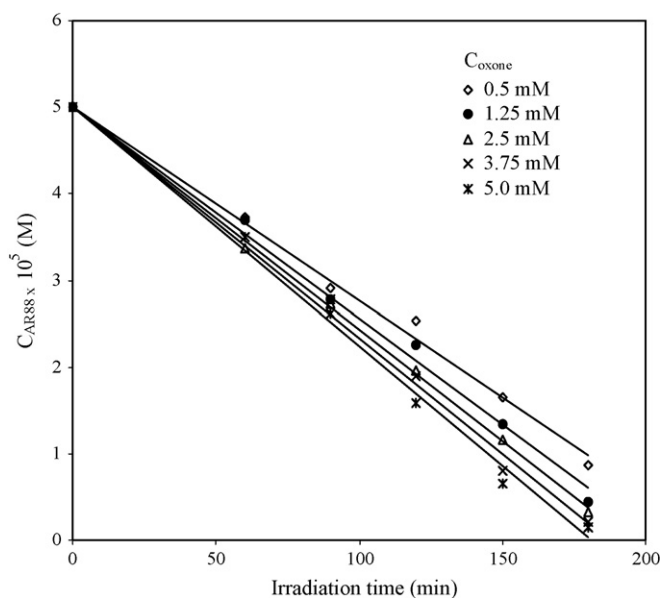Fig. 8. Decolorization of acid red 88 solutions at different oxone concentrations: $C_{AR88} = 0.05$ mM; $C_{Cu^{2+}} = 0.025$ mM.

decolorization in 2 h of irradiation was achieved with the highest $C_{Cu^{2+}}$ (0.075 mM) employed in our study.

3.2.3. Variation of oxone concentration

The effect of amount of oxone addition on the decolorization of the dye by Cu^{2+}/oxone system was investigated by varying the concentration of oxone from 0.5 to 5 mM while maintaining other experimental conditions constant. The observed pseudo-zero-order rate constants at different concentrations of oxone are depicted in Fig. 9. It is inferred from Fig. 9 that the rate constant increases sharply with low concentrations of oxone, viz., 0.5 mM and only a slight increase in the degradation rate was observed on further increase in C_{oxone}. This may be due to

the destruction of sulphate and hydroxyl radicals by the excess HSO_5^- as the concentration of the latter is increased.

3.3. Efficiency of Fe^{3+} over Cu^{2+} for the photocatalyzed degradation of AR88

3.3.1. Decolorization studies

A comparative study on the efficiency of the metal-ions (Cu^{2+} and Fe^{3+}) for the photocatalyzed degradation of AR88 was made from the experimental data obtained under identical conditions [$C_{AR88} = 0.05$ mM; $C_{oxone} = 1.25$ mM; $C_{Fe^{3+}} = C_{Cu^{2+}} = 0.025$ mM] and the results are shown in Fig. 10. The optimum oxone concentration observed in the kinetic and decolorization studies was 0.5 mM. However, in order to achieve higher mineralization rate, we have used 1.25 mM concentration of oxone since the addition of lower amount of oxone takes longer irradiation times. In the absence of any metal-ion, only 8% decolorization of AR88 was observed in 30 min. However, it can be observed that about 91% decolorization of the dye takes place in 10 min with Fe^{3+} ion (0.025 mM) as a catalyst whereas 15% decolorization of the dye in 30 min could be achieved with Cu^{2+} ion (0.025 mM). The greater efficiency of Fe^{3+}/oxone over Cu^{2+}/oxone reagent may be attributed to the formation of stable complex [AR88···Fe^{3+}] which absorbs the visible light and effectively produces AR88$^{\bullet+}$, Fe^{3+} (that later turns to Fe^{2+}) and organics which on further oxidation in the presence of oxidant might lead to its successive degradation. In the case of Cu^{2+}/oxone system, due to the less stability of the complex [AR88···Cu^{2+}], the enhancement in the dye degradation rate is less. Barb et al. [11] investigated the catalytic decomposition of H_2O_2 by various metal-ions and reported that the catalytic decomposition of H_2O_2 by Cu^{2+} ion is 25 times slower than the corresponding reactions involving Fe^{3+} ion. Aguiar and Ferraz [36] reported that during the Azure B degradation by Fenton-like reactions iron-containing
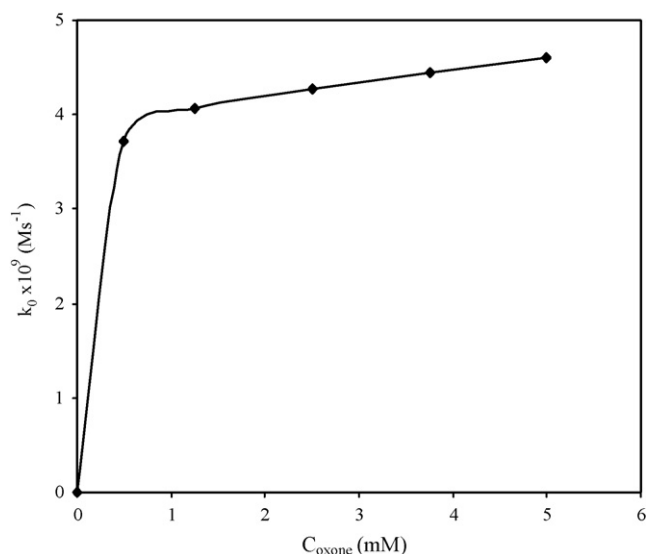

Fig. 9. Plot of pseudo-zero-order rate constant vs. oxone concentration for the decolorization of acid red 88 (0.05 mM) in presence of Cu^{2+} ion (0.025 mM).
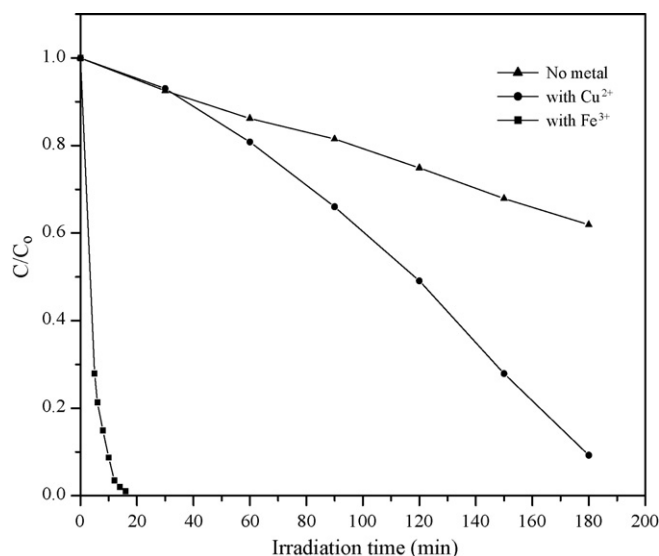

Fig. 10. Comparison of efficiency of metal-ions for the decolorization of acid red 88: $C_{AR88} = 0.05$ mM; $C_{Fe^{3+}} = C_{Cu^{2+}} = 0.025$ mM; $C_{oxone} = 1.25$ mM.

reactions consume substantially more H_2O_2 than reactions containing copper.

3.3.2. Mineralization studies

Since the intermediate products of some organic compounds can sometimes be more toxic than the original compound itself, mineralization of the compound should be ensured before discharging the polluted waters into the ecosystem. The mineralization of the pollutant can be obtained by monitoring the TOC of the treated solutions. The efficiency of metal-ion would be obtained by comparing the TOC values observed for the dye degradation and mineralization in both Cu^{2+}/oxone and Fe^{3+}/oxone systems. The plot of TOC_t/TOC_0 against irradiation time is presented in Fig. 11. From the Fig. 11 two significant points emerge, viz., (a) mineralization process starts or becomes important after the decolorization process has been almost completed and (b) the TOC reduction in 180 min of irradiation is only 11.8% in the case of Cu^{2+} whereas it is 77.4% when Fe^{3+} ions are used. Thus, TOC analysis further confirms the efficiency of Fe^{3+} over Cu^{2+} for the photocatalyzed degradation of the acid red 88. It can also be understood that greater extent of mineralization will be obtained on prolonged visible light irradiation. The detailed mechanism of mineralization using M^{n+}/oxone reagent where $M^{n+} = Fe^{3+}$ or Cu^{2+} is presented in the following section.

3.4. Mechanism

Based on the experimental observations, the following reaction mechanism is suggested for the visible light-assisted mineralization of dyes using Fe^{3+} or Cu^{2+}/oxone reagent:
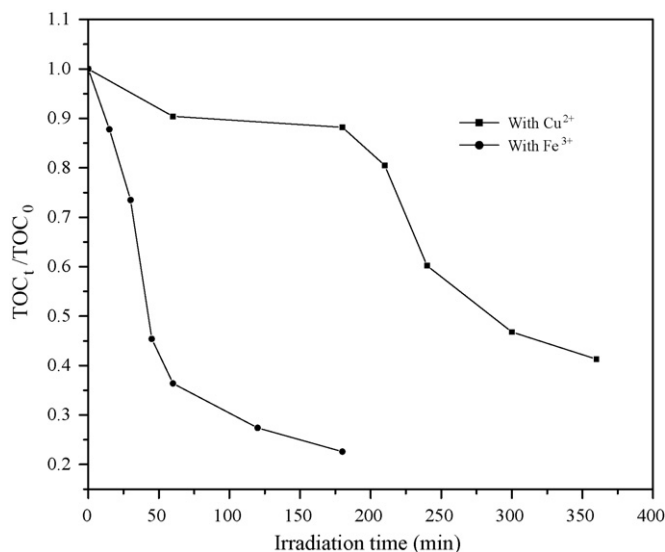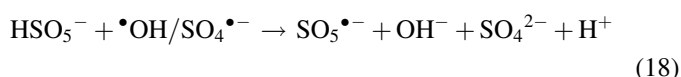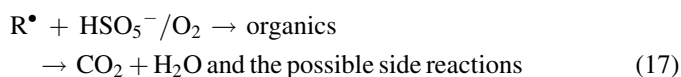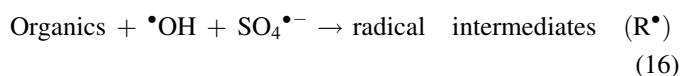
$$[AR88] + h\nu \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [AR88]^* \tag{5}$$

Fig. 11. Comparison of efficiency of metal-ions for the mineralization of acid red 88: $C_{AR88} = 0.05$ mM; $C_{Fe^{3+}} = C_{Cu^{2+}} = 0.025$ mM; $C_{oxone} = 1.25$ mM.

$$AR88^* + HSO_5^- \xrightarrow[k_2]{Slow} \begin{cases} AR88^{\bullet+} + {}^\bullet OH + SO_4^{2-} & (6a) \\ AR88^{\bullet+} + OH^- + SO_4^{\bullet-} & (6b) \end{cases}$$

$$AR88 + M^{\delta+} \rightarrow [AR88\cdots M^{\delta+}],$$
$$\text{where } M^{\delta+} = Fe^{3+} \text{ or } Cu^{2+} \tag{7}$$

$$[AR88\cdots Fe^{3+}] + h\nu \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} [AR88\cdots Fe^{3+}]^* \tag{8}$$

$$[AR88\cdots Fe^{3+}]^* + HSO_5^- \xrightarrow[k_4]{Slow} \begin{cases} AR88^{\bullet+} + Fe^{3+} + {}^\bullet OH + SO_4^{2-} & (9a) \\ AR88^{\bullet+} + Fe^{3+} + OH^- + SO_4^{\bullet-} & (9b) \end{cases}$$

$$[AR88\cdots Cu^{2+}] + h\nu \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} [AR88\cdots Cu^{2+}]^* \tag{10}$$

$$[AR88\cdots Cu^{2+}]^* + HSO_5^- \xrightarrow[k_6]{Slow} \begin{cases} AR88^{\bullet+} + Cu^{2+} + {}^\bullet OH + SO_4^{2-} & (11a) \\ AR88^{\bullet+} + Cu^{2+} + OH^- + SO_4^{\bullet-} & (11b) \end{cases}$$

$$AR88^{\bullet+} + HSO_5^- \rightarrow organics + OH^- + SO_4^{\bullet-} \tag{12}$$

$$AR88^{\bullet+} + Fe^{3+} \text{ or } Cu^{2+} \rightarrow organics + Fe^{2+} \text{ or } Cu^+ \tag{13}$$

$$2Fe^{2+} \text{ or } 2Cu^+ + HSO_5^- \rightarrow 2Fe^{3+}$$
$$\text{or } 2Cu^{2+} + SO_4^{2-} + OH^- \tag{14}$$

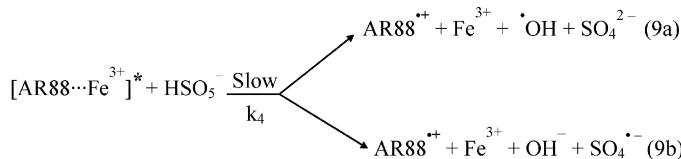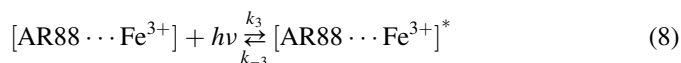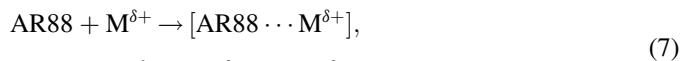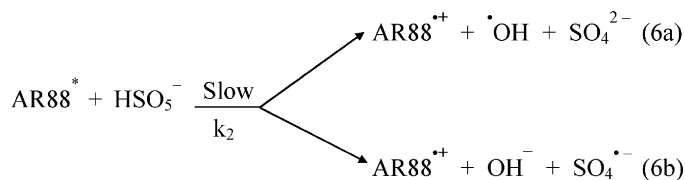$$Fe^{3+} + OH^- \rightarrow Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + {}^\bullet OH \tag{15}$$

$$Organics + {}^\bullet OH + SO_4^{\bullet-} \rightarrow radical \quad intermediates \quad (R^\bullet) \tag{16}$$

$$R^\bullet + HSO_5^-/O_2 \rightarrow organics$$
$$\rightarrow CO_2 + H_2O \text{ and the possible side reactions} \tag{17}$$

$$HSO_5^- + {}^\bullet OH/SO_4^{\bullet-} \rightarrow SO_5^{\bullet-} + OH^- + SO_4^{2-} + H^+ \tag{18}$$

$$R^\bullet + O_2 \rightarrow R-OO^\bullet \tag{19}$$

In the above mechanism, the formation of metal complexes has been reported [37]. The change in the absorption spectrum of the dye observed when a metal-ion was introduced to the dye solution is added evidence to the above fact. The electrons donated by the excited dye or dye–metal ion complex is accepted by the oxone and leads to the formation of ${}^\bullet OH$ and $SO_4^{\bullet-}$ radicals and OH^- [13]. The formation of ${}^\bullet OH + SO_4^{2-}$ or $OH^- + SO_4^{\bullet-}$ (Eqs. (6a), (6b), (9a), (9b), (11a), (11b)) are based on the electron-pulse radiolytic studies, $HOOSO_3^- + e^-_{aq}$ by

Hart [14] and Maruthamuthu and Neta [35]. It is also estimated by the above workers that the possibility of formation of a:b in reactions (6a), (6b), (9a), (9b), (11a) and (11b) is 4:1. The dye radical cation formed reacts with oxone and the metal-ions to form simple degradation products (Eqs. (12) and (13)). Oxone regenerates the catalyst and it produces $^\bullet OH$ in the next step which assists for the faster degradation of the dye. Further, Cu^{2+} being a weaker oxidizing agent, the radical oxidations to organics, namely, $AR88^{\bullet+}$ to organics, by Cu^{2+} (Eq. (13)) is limited [38], and oxidation of $AR88^{\bullet+}$ to organics mainly takes place via Eq. (12). So, the formation of more $^\bullet OH$ is limited in Cu^{2+}/oxone system and it is the reason for the very low degradation rate observed in this system. At the same time, it is not possible to ignore the formation of complexes between the degradation products formed and Fe^{3+} or Cu^{2+} reacting further with oxone [18,39,40]. Eqs. (16) and (17) show chain oxidative reactions due to radical intermediates. The formation of less reactive radical species $SO_5^{\bullet-}$, by the reactions of $^\bullet OH$ and $SO_4^{\bullet-}$ with oxone (Eq. (18)) may also compete with reaction (16) [35]. This is the reason for the decrease in the reaction rate with higher concentrations of oxone used in our study. Reaction of the radical ($R^\bullet$) with dissolved oxygen leading to the formation of peroxy radicals, $R-OO^\bullet$ (R = H, alkyl, aryl), which are important and react with the rate constants of ca. $10^9 \, M^{-1} \, s^{-1}$ close to the diffusion control limit in aqueous solutions [41] is also possible. These peroxy radicals serve as chain propagators and oxidize organic materials either by hydrogen abstraction or by electron transfer processes [42,43].

4. Conclusions

Decolorization of AR88 in Cu^{2+}/oxone system was found to follow zero-order kinetics with respect to the dye, and first-order kinetics in Fe^{3+}/oxone system. In both cases, decolorization of AR88 was seen to be accelerated with higher concentrations of metal-ions in solution. When using 0.075 mM concentration of the metal-ions, almost 95% decolorization is attained in about 2 h with Cu^{2+} ion and in about 14 min with Fe^{3+} ion. A rapid decolorization and TOC removal rates obtained with Fe^{3+} reveal Fe^{3+} as the efficient catalyst over Cu^{2+} ion for the photocatalyzed degradation of AR88 in presence of oxone. A suitable mechanism involving initial complex formation between Fe^{3+} ion or Cu^{2+} ion and AR88 is suggested to explain the observed photocatalyzed degradation of AR88.

Acknowledgements

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